

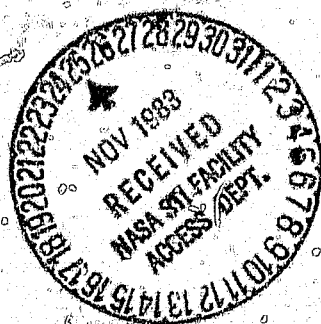
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Evaluation and Prediction of Long-Term Environmental Effects on Nonmetallic Materials

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MARTIN MARIETTA

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Final
Report

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**EVALUATION AND PREDICTION OF
LONG-TERM ENVIRONMENTAL
EFFECTS OF NONMETALLIC
MATERIALS**

**MARTIN MARIETTA AEROSPACE
DENVER AEROSPACE
P.O. Box 179
Denver, Colorado 80201**

FOREWORD

This is a final report for the second phase of the program, Evaluation and Prediction of Long-Term Space Environmental Effects on Nonmetallic Materials, conducted by Martin Marietta for the National Aeronautics and Space Administration, Marshall Space Flight Center, under contract NAS8-33578.

The program was conducted in the Mechanical Materials Engineering Section with Mohan Misra as Program Manager and Harold Papazian as Principal Investigator. Contributors to the program included W. J. Arbogast and C. E. Forsyth for material tests.

Up to the time of his unfortunate demise, Charles Peacock of NASA-MSFC served as program monitor. Dr. Ray Gause and Ms. Ann Whitaker served as technical advisors.

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I. INTRODUCTION

Although nonmetallic materials are generally recognized as being susceptible to the changes caused by the environments associated with long-life spacecraft, data concerning the effects of irradiation and long-term thermal-vacuum exposure on the specific mechanical, electrical, and thermal properties of such material have not been readily available. Because the performance and life of any structure, system or component directly depends on the integrity of the materials used in its construction, the ability of these materials to withstand the operating environment is of utmost importance in meeting service life requirements.

The degradation of any material or material system, even if slow at normal-use temperatures, can lead to failure over a long period. For example, in a polymer system used as a structural member, the accumulated changes may eventually lead to loss of integrity. Real-time tests of materials that may be used in a system can be clearly impractical in time and money. If short-time tests can be used to predict future behavior, these tests can considerably enhance mission success.

The primary emphasis of the preceding phase of this program was on the effects of long-duration thermal-vacuum exposure and had its foundation in the Viking materials qualification program of some 10 years ago. The project established the requirements for materials suitable for the Viking spacecraft. Specimens of the same materials that had remained in a thermal-vacuum environment to the present time were tested to determine whether any changes in material properties had occurred over the long-term exposure. In general the largest changes occurred in such electrical properties as dielectric strength, dielectric constant and volume resistivity. The mechanical properties showed only small changes—some increasing and others decreasing in strength. The preceding phase thus established the important fact that thermal-vacuum exposure would not degrade the structural integrity of a spacecraft constructed with nonmetallic material systems.

The present phase of the program was primarily devoted to the effects of charged particle irradiation on the mechanical properties of graphite/epoxy composites. There is a paucity of literature data⁽¹⁾ concerning the charged particle irradiation effects on such composites, and it is essential that this task be performed as soon as the accelerator becomes available. The test results obtained to date are the baselines to be used later for comparison with results after irradiation. In preparation for the future testing, Section V discusses in considerable detail the effects that may be observed.

Considerable effort was devoted to development of models and accelerated test methods useful for predicting material behavior. Zhurkov's approach to the strength of solids is a useful first step toward such predictions. This is discussed in considerable detail showing the underlying fundamentals of the approach as well as its application to accelerated testing of composites.

II. PROGRAM OBJECTIVE

The objective of this program is to continue the experimental evaluation of changes in the functional properties of a number of nonmetallic materials as a function of simulated space environments and to use such data to develop models for accelerated test methods useful for predicting such behavioral changes.

Another objective is to evaluate the effects of charged particle irradiations on candidate space materials.

III. TECHNICAL APPROACH

A. TASKS

Task 1 requires evaluation of the final 20 Viking specimens. These were to be irradiated and the results compared with the preirradiated results obtained in the first phase of the program.

Task 2 requires testing graphite/epoxy specimens prepared by Hercules. Sixty-four in-plane shear specimens were to be tested--20 baseline specimens, 20 specimens to be tested after exposure to thermal-vacuum, and 24 specimens to be tested after irradiation of specimens that had undergone the thermal-vacuum exposure.

Task 3 requires testing of graphite/epoxy specimens prepared by MSFC that had undergone thermal-vacuum exposure for some six years at MSFC. They were of four different configurations for appropriate mechanical property tests. These were tensile, interlaminar short beam shear, flexure, and compression strength. Twenty-three specimens were to be tested as a thermal-vacuum-exposed baseline and 41 specimens were to be tested after irradiation by MSFC.

Task 4 requires testing of thermal-vacuum-exposed specimens after charged particle irradiation.

Task 5 requires comparison of pre- and postexposure data for the materials previously described and an attempt to develop analytical models for predicting the long-term environmental degradation of selected material properties. Expected irradiation effects and predictive testing are discussed in considerable detail.

A total of 64 graphite/epoxy specimens were tested for baseline (preirradiation) data, and a total of 84 specimens were to be tested after undergoing irradiation. Of the latter, 20 were Viking specimens and 64 were to be graphite/epoxy for comparison with the preirradiation baseline results.

B. TEST PROCEDURES

The most important aspect of the MSFC program is the fact that once a specimen enters the thermal-vacuum environment, it is never again exposed to the ambient environment. All specimens are transferred between the thermal-vacuum system, the irradiation chamber, and final transfer to the in situ vacuum chamber under a vacuum environment. This is done by transferring canisters containing specimens under vacuum to various systems and finally through the airlock of the test chamber. The importance of this approach is demonstrated in Section V.A.

All tests were conducted according to appropriate ASTM test methods and are designated in the appropriate table headings in Section IV.

C. SPECIMEN DESCRIPTIONS

The Hercules graphite/epoxy specimens were #45 degrees in-plane shear of 4- and 8-ply AS4/3501-6 and HMS/3501-6 materials. The specimens designated in Table 2 (Section IV) as 004 and 005 were of AS4/3501-6 with 6k tows and 12-mil and 21-mil thickness, respectively. The specimens designated as 009 and 010 were of HMS/3501-6 with 12k tows and 12-mil and 21-mil thickness, respectively.(2)

The graphite/epoxy composites, Type 37 etc, were prepared by MSFC some six years ago and remained under thermal-vacuum exposure through testing. At present the preparations for the various types are not available. Within the four configurations, the types selected for testing included those with enough specimens for meaningful comparisons between baseline and irradiation tests.

IV. RESULTS

All values reported in the following tables are the averages of several specimens. The \pm values indicate the maximum spread from the average and are probably attributable to differences in specimen thicknesses. Only the average thickness is given in the tables.

Table IV-1 shows the results for the Hercules graphite/epoxy specimens under in-plane shear. In all cases modulus increased after a year under thermal-vacuum exposure. (Five samples of each specimen type were tested.) This is probably attributable to further curing and/or outgassing of a plastisizing agent of some kind. Although the change in ultimate strength of the AS4/3501-6 (004, 005) may not be significant, the changes for the HMS/3501-6 material (009, 010) are large enough to be considered significant. Table IV-2 shows the resin contents of these materials. The TGA method is much simpler than the standard acid decomposition method, and we consider it to be more nearly representative of the true resin content. Comparison of these results with those in Table IV-1 shows that the decrease in ultimate for both materials is associated with the smaller amount of resin content. If this is real, a significant observation has been made and suggests more testing in this direction for in-plane shear studies.

Tables IV-3 through IV-6 presents results for the specimens prepared at MSFC that were under thermal-vacuum exposure for some six years. These results serve as a baseline for comparison with the postirradiation tests to be performed in the next phase of this work.

Table IV-3 shows the results of tensile testing. Assuming the same resin was used and noting the difference in thickness, it must be concluded that two different fibers were used in the two types.

Table IV-4 shows the apparent shear strength of Type 37, and Table IV-5 shows the flexure strength of Type 38. These will serve as baselines for later irradiation tests.

Table IV-6 shows the results of compression testing. Some results with electron irradiation obtained during the last phase of the program have been included. Because epoxy resins undergo crosslinking under irradiation, the behavior of Type 26 is as expected—an increase in strength after irradiation. Only two specimens of Type 38 were irradiated and the slight decrease in strength may not be significant. If much less resin were used than for Type 26, the decrease could also be attributed to that fact.

In conclusion, a much larger number of specimens must be tested than has been possible to date, and much better quality control during specimen preparation and irradiation must be exercised. Similar comments have been made by others.

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Table IV-1 Hercules Graphite/Epoxy Tensile Strength (ASTM D3410)

Specimen	Baseline		1-Year Thermal-Vacuum Exposure		% Change of Averages	
	Ultimate, ksi	Modulus x 10 ⁶	Ultimate, ksi	Modulus x 10 ⁶	Ultimate	Modulus
AS4/3501-6						
004 4-ply/12.3 mils	24.4 ^{+1.6} -2.2	2.37	25.2 ^{+2.0} -1.4	2.49	+3	+5
005 8-ply/21.3 mils	24.8 ^{+1.7} -2.3	2.62	24.3 ^{+1.9} -2.7	3.02	-2	+15
HMS/3501-6						
009 4-ply/12 mils	10.4 ^{+1.2} -1.4	2.33	11.5 ^{+0.8} -1.5	3.00	+11	+29
010 8-ply/21.3 mils	12.7 ^{+0.5} -1.3	2.51	11.5 ^{+1.0} -0.5	2.55	-9	+2

Table IV-2 Resin Content

Series	Hercules Data, %	TGA (Martin Marietta), %
004	33.4	27.4
005	26.9	22.8
009	28.4	28.0
010	24.8	25.4

Table IV-3 MSFC Graphite/Epoxy Tensile Strength (ASTM D2990)

Specimen	Ultimate, ksi	Modulus x 10 ⁶	% Elongation
Type 36 (62 mils)	27.1 ^{+9.5} -8.3	6.04 ^{+0.6} -0.77	0.81 ^{+0.4} -0.46
Type 41 (36 mils)	36.7 ^{+10.7} -7.3	6.14 ^{+0.39} -0.63	1.07 ^{+0.53} -0.33

Table IV-4
MSFC Graphite/Epoxy Interlaminar
Short Beam Shear Strength (ASTM
D2344)

Specimen	Apparent Shear Strength, ksi
Type 37 (88 mils)	6.67 ^{+0.45} -0.23

Table IV-5
MSFC Graphite/Epoxy Flexure
Strength (ASTM D790)

Specimen	Maximum Fiber Strength, ksi
Type 38 (120 mils)	56 ^{+7.4} -1.2

Table IV-6
MSFC Graphite/Epoxy Compression Strength (ASTM
D3410)

Specimen	Compression Strength, ksi	
	6-Year Thermal-Vacuum Exposure	After Irradiation
Type 24 (80 mils)	33.9 ^{+3.6} -2.5	
Type 26 (90 mils)	29.7	46.7 ^{+10.0} -7.7
Type 37 (90 mils)	44.2 ^{+10.5} -7.2	
Type 38 (100 mils)	52.2 ^{+7.4} -3.4	47.5 ^{+2.8} -2.8
Type 40 (61 mils)	40.5 ^{+12.4} -10.8	
Type 42 (62 mils)	44.2 ^{+10.2} -9.4	

V. ANALYSIS

A. IRRADIATION DAMAGE ESTIMATES

Although the experimental portion of irradiation damage was not completed, the expected results were assessed in preparation for the test results.

The most important effects of irradiation in polymers are crosslinking and degradation. If crosslinking predominates, the ultimate effect of irradiation will be to produce a network polymer in which all molecules are joined to each other. If degradation predominates, the molecules become smaller and smaller as irradiation proceeds and the material loses its polymeric properties.

The degree of unsaturation of a polymer can also change on irradiation. Polymers that are initially highly unsaturated tend to become less so on irradiation, while with initially saturated polymers the amount of unsaturation increases with dose. The formation of an unsaturated double bond will tend to labilize the bonds (free to move) in the allyl position, leading to a conjugated double bond system. Such an effect accounts for the coloration of some polymers on irradiation. Another important change is the formation of gas during irradiation. The amount of gas produced depends on the polymer, dose, temperature, type of irradiation, etc.

The free radicals (highly labile molecular fragments) formed during irradiation⁽³⁾ must play an important part in chemical changes. These free radicals can be both short-lived and long-lived depending on the polymer. The response of polymers to irradiation is markedly affected by the presence of other substances, most probably from reaction with the free radicals produced. Oxygen produces a marked effect, usually a decrease in the tendency to crosslink, i.e., oxygen reaction with the broken bonds (of long-lived radicals) rather than crosslinking. Thus any irradiation study that allows the sample to be exposed to the ambient environment after irradiation must be suspect. (The experimental methods of MSFC overcome such concerns because the specimens are never exposed to ambient.) The amount of oxygen initially present in the material causes only a small effect. Large effects can occur if the sample is thin enough and the dose rate is low enough for oxygen to diffuse during the irradiation.

To produce marked changes in most polymeric materials requires roughly one chemical change per molecule. A dose of R rads (1 rad = 100 ergs/gm) on a molecule of M molecular weight deposits an average of

$$(R \times 100 \text{ ergs/gm}) \left(\frac{M \text{ gm mole}^{-1}}{6.02 \times 10^{23} \text{ molecules mole}^{-1}} \right) \left(\frac{1}{1.602 \times 10^{12} \text{ ergs eV}^{-1}} \right) =$$

$$= 1.04 \times 10^{-10} (RM) \text{ eV/molecule.}$$

Denoting the chemical changes per 100 eV as G, the dose needed to achieve a change is

$$R = \left(\frac{100}{G} \right) \left(\frac{0.96 \times 10^{10}}{M} \right) = \frac{0.96 \times 10^{12}}{GM} \text{ rads.}$$

In all but exceptional cases G ranges between 1 and 5. Taking M = 2000 and G = 1 yields R = 4.8×10^8 rads. For the worst case with G = 5, R = 0.6×10^8 rads. In any long-duration flight these doses are easily obtained.

Figure 1 shows the penetration depth as a function of dose in a 30-year geostationary orbit for an organic composite.⁽⁴⁾ It is represented by an exposure of approximately 10^{11} rads at 0.5- μ m (0.02-mil) depth to low-energy protons and approximately 5×10^9 rads at 50- μ m (0.2-mil) depth due to electrons. As expected, energy deposition decreases with depth in the material and shows that a 30-year flight doses on the order of 10^8 rads would cause changes as deep as 100 mils in relatively thick composites.

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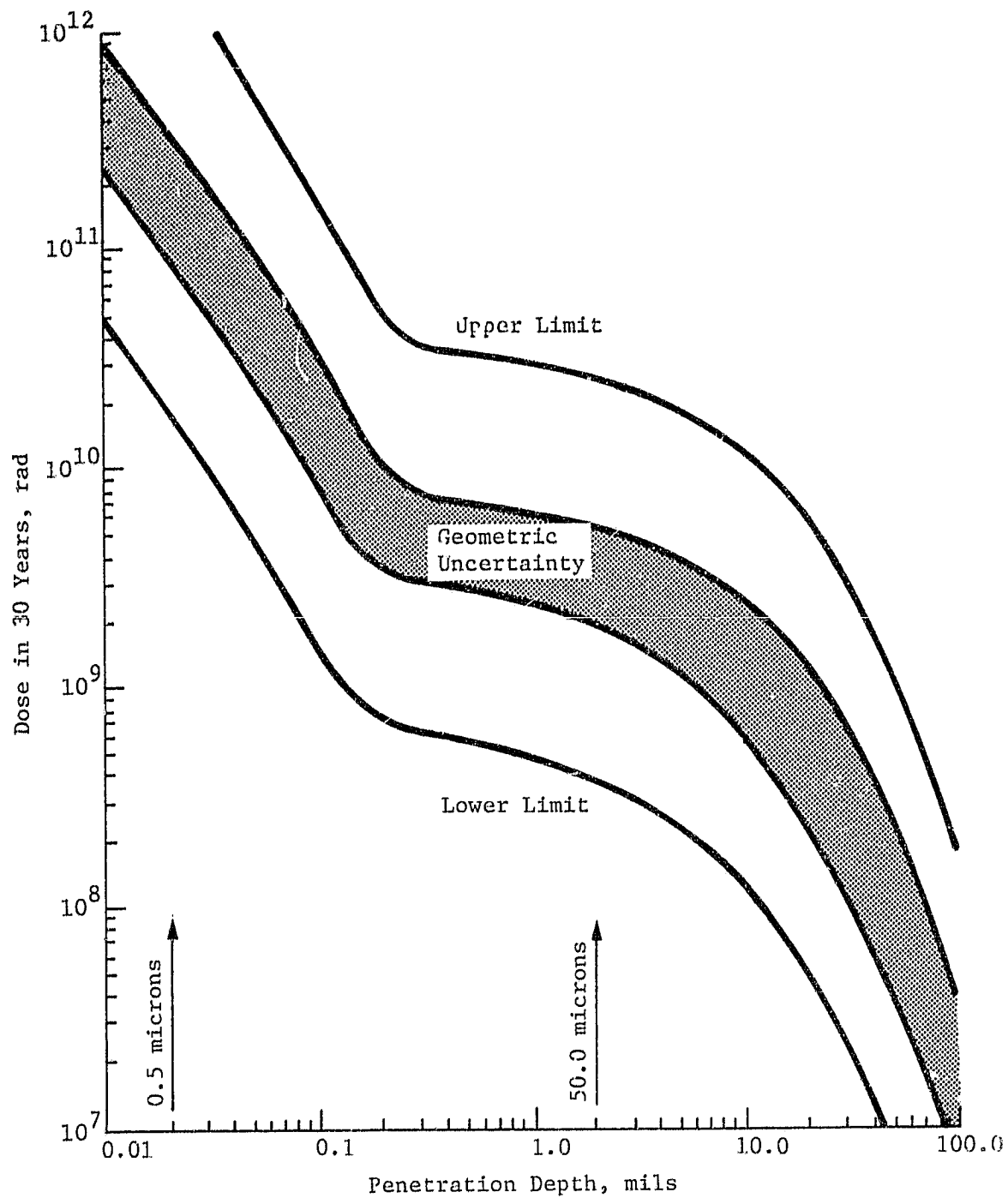


Figure V-1 Penetration Depth As a Function of Dose in Geostationary Orbit

Figure 2 shows a decay rate analysis (developed from data in Ref 5) of free radicals in an epoxy resin (TGDDM-DDS) at room temperature after electron irradiation. Clearly long-lived radicals are present. As previously discussed, if after irradiation specimens are exposed to the ambient environment before testing, the results must be questioned. The MSFC approach avoids this concern by never exposing specimens; the figure confirms the importance of our approach.

Only one cursory reference to proton irradiation was revealed by a literature search(1). After 756 hours at 10^{-6} torr with 4 suns UV radiation and 10 minutes 1-MeV proton irradiation (dose not given), HT-S/X-904 showed no change in flexure, but shear decreased by 14 percent. GY-70/X-904 showed a 10 percent decrease in flexure but only a 1.5 percent decrease in shear. It should be emphasized that these changes may be associated with the UV radiation because no tests with only UV were performed. Using 1-MeV electrons instead of protons, a 12 percent decrease in flexure and a 19 percent decrease in shear was observed with HT-S/X-904, while GY-70/X-904 showed a 21 percent increase in flexure and a 3 percent increase in shear.

The flexure properties of miniature (22 x 13 x 0.51-mm) unidirectional specimens of T300/5208 composite were exposed to electron irradiations(3) with doses up to 8×10^9 rads. The strength increased slightly with dose (approximately 4 percent), while the modulus was unaffected. Statistically, however, the limits for the 95 percent confidence led to uncertainty in the location of the mean. The authors suggested the possibility of large, perhaps significant, changes in flexure and emphasized the need for quality control in specimen preparation and testing.

These comments demonstrate the paucity of literature data concerning the effects on composites as well as the uncertainty of available results and the importance of the MSFC program.

A further consideration (generally not discussed) is the radiation of a mechanical property while under load such as might occur during reorientation or change of orbit. Figure 3 shows such an effect on the creep rate of polystyrene developed from data given in Reference 6. It may be of value to consider such phenomena in some further phase of the program.

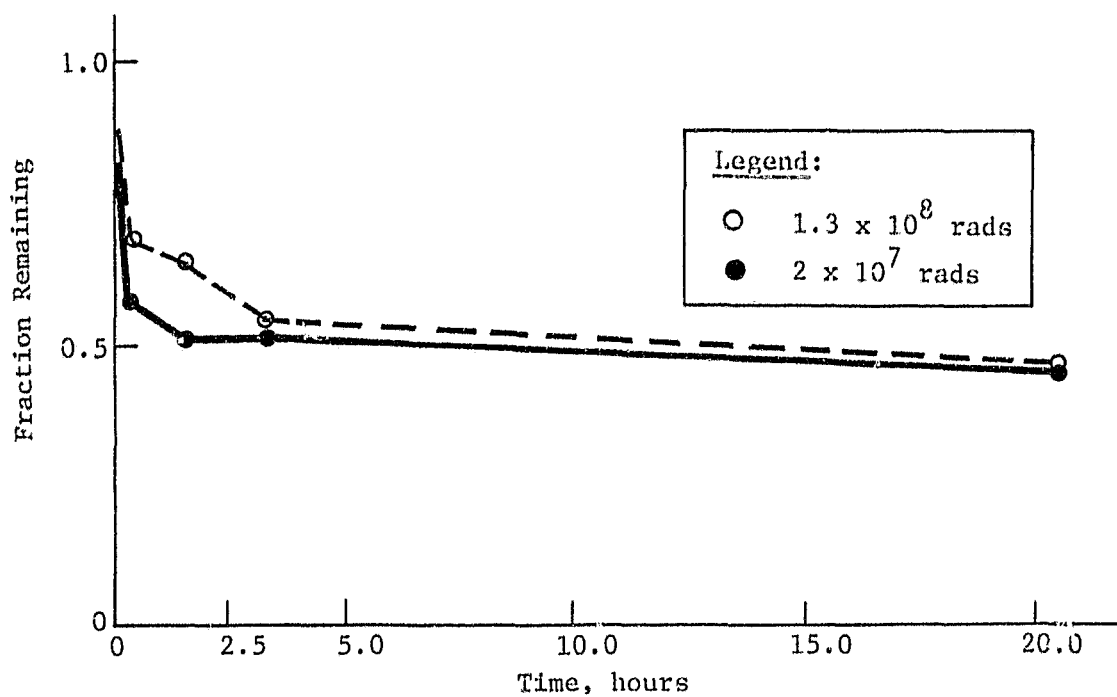


Figure V-2 Free Radical Decay After Electron Irradiation Showing Long-Lived Species

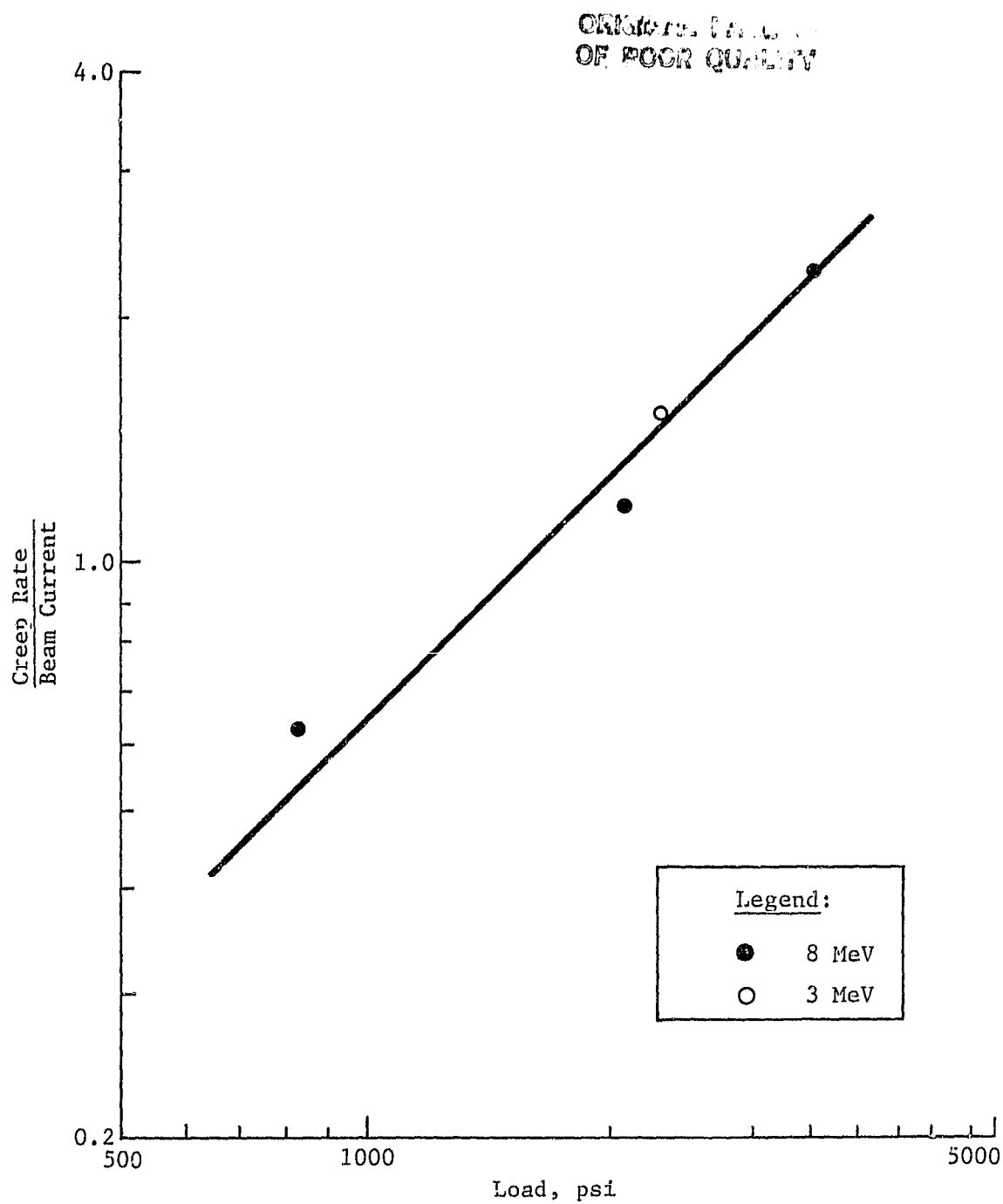


Figure V-3
Effect of Dose Rate on Creep Rate As a Function of Load During Electron Irradiation

B. ZHURKOV'S APPROACH TO THE STRENGTH OF SOLIDS FOR PREDICTIVE MODELING

The mechanisms and the laws governing the failure of brittle solids and polymers have features in common and understanding the phenomena can lead to successful development of accelerated tests for such materials. For long-duration performance of materials, the designer needs to have data on how long his choice of material can be expected to last in a given situation. Real-time tests are clearly impractical in both time and money, and the obvious solution to the problem is to use an acceptable accelerated test to predict lifetime.

The time dependence of the strength of solids and its connection with the mechanism of failure was studied by Zhurkov⁽⁷⁾ and his coworkers. His phenomenological approach to delayed failure (creep rupture) is also known as kinetic rate theory. In the Soviet Union the Zhurkov method is unquestioned⁽⁸⁾ while in the West it has been suspect leading to questioning of the method with such comments as "... a good bit of discretion is often required to force the data to intersect at a pole."⁽⁹⁾ The purpose of the present discussion is to minimize the discretion.

The Zhurkov method has modifications under certain conditions that have not been recognized. In some materials the common pole σ_0 , which is obtained from $\log \tau$ vs σ data at several temperatures, is much larger than $\tau_0 \sim 10^{-13}$ seconds obtained with materials that conform to the usual Zhurkov method. Zhurkov associated τ_0 with the vibration frequency of the bonded atoms in the solid. In other instances experimental data do not result in a common pole at all. The following discussion shows how these materials can be brought into the Zhurkov framework.

From an applied viewpoint, the primary value of the Zhurkov method is that it may be used to devise accelerated testing of materials. Here such tests are outlined for creep rupture within the usual method and its modifications. The following section shows that accelerated tests for composites under static, dynamic and cyclic loads are also possible.

Zhurkov developed his creep rupture method by successfully applying his relationships to a variety of materials (metals and nonmetals) and their time dependence of strength under unidirectional tension.

The relationships and definitions of Zhurkov are:

$$[1] \quad \tau = Ae^{-\alpha\sigma} \text{ (at constant temperature)}$$

$$[2] \quad \tau = \tau_0 e^{U^*/kT} \text{ (at fixed } \sigma)$$

where

τ = time to rupture,

α = constant,

A = constant,

σ = applied uniaxial stress,

τ_0 = constant,

$U^* = U_0 - \gamma\sigma$ (energy),

U_0 = an activation energy,

γ = constant,

k = Boltzmann's constant,

T = absolute temperature.

When a material behaves according to Equations [1] and [2], τ_0 is considered to be the period of natural oscillation, i.e., $\tau_0 = 1/\nu$ where ν is the vibrational frequency of the bonded atoms; U_0 is the activation energy of the elementary act of failure in the absence of stress; and γ is a coefficient that depends on the structure of the material. Equations [1] and [2] are related through

$$[3a] \quad \alpha = \gamma/kT$$

$$[3b] \quad A = \tau_0 \exp(U_0/kT).$$

Figure 4 shows a schematic of results obtained by applying Equation [1] to creep rupture data. Such results are typical of those obtained by Zhurkov for a variety of materials. From such results, the constants A and α are obtained at each temperature that is studied.

Figure 5 shows a schematic of results obtained by applying Equation [2] to such data where the slopes equal $U^*/2.303k$. A U^* is obtained for each σ . Then a plot of U^* vs σ yields $U^* = -\gamma\sigma + U_0$, where the slope is γ and the intercept U_0 . It should be noted that γ may also be obtained from Equation [3a].

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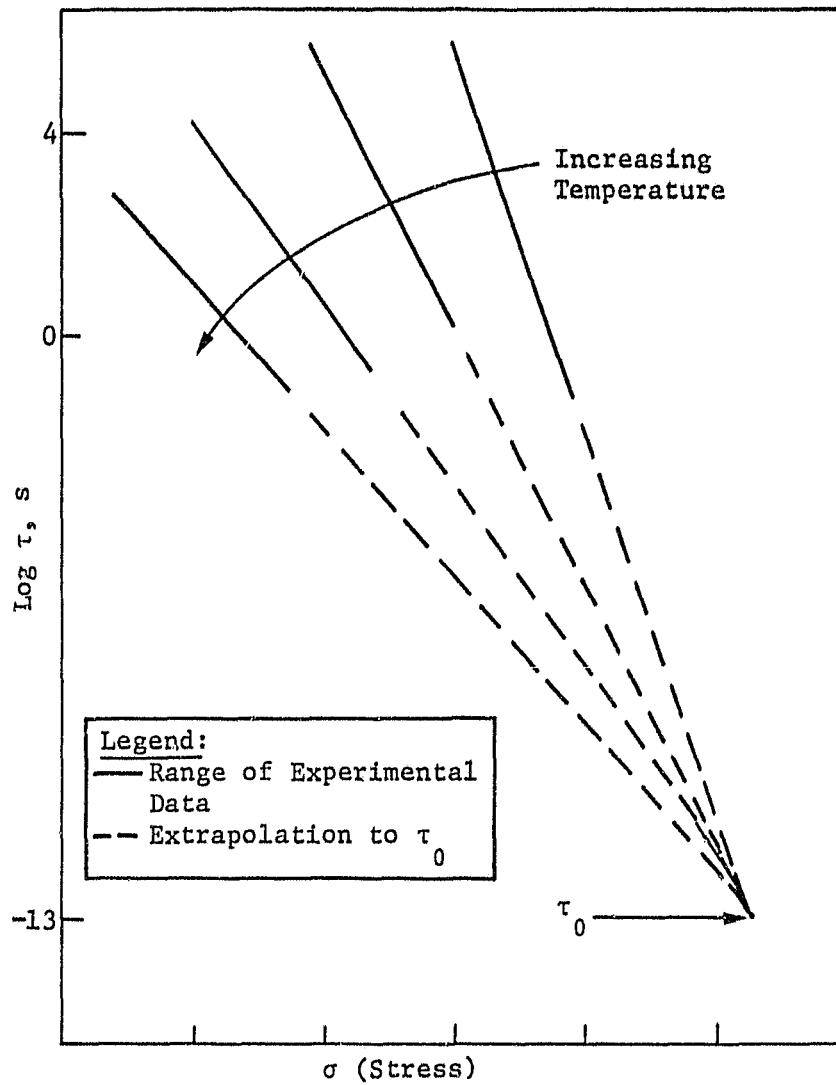


Figure V-4 Application of Zhurkov's Equation [1]

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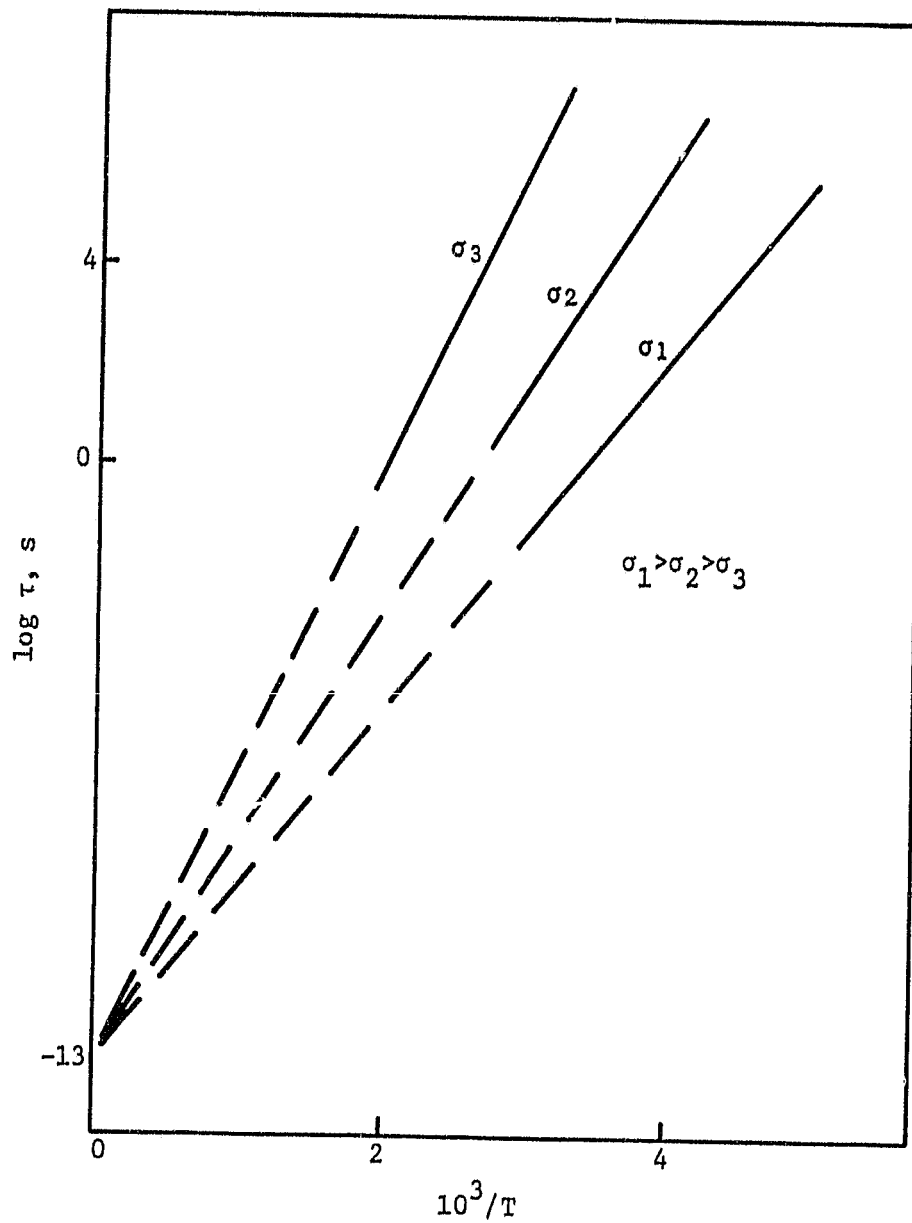


Figure V-5 Application of Zhurkov's Equation [2]

Data similar to Figures 4 and 5 for viscose fiber may be found in Chapter 1 of Reference 8 and are analyzed in complete accord with the Zhurkov method.

Thus for an accelerated test of creep rupture, at some temperature of interest three or four points at relatively high stresses (short rupture times) will permit predictions of results at much lower stresses, i.e., at much longer times to rupture. Such data taken at two or three easily accessible temperatures should predict results for desired stress at, say, very low temperatures. Such applications are the claimed usefulness of the method, and have indeed been applied to many materials.⁽⁸⁾

In Chapter 1 of Reference 8 the time dependence of the strength of Celluloid at four temperatures (20, 70, 85 and 100°C) is presented (without discussion) in a figure similar to Figure 4 here. However, the pole τ_0 , occurs near 5×10^{-4} seconds--some nine orders of magnitude removed from normal vibrational frequencies for well-behaved Zhurkov materials. From these data then, Equation [3b] is $A = 5 \times 10^{-4} \exp(U_0/RT)$. Here and below, R will be used rather than k and the energy terms will be in calories.

The data for Celluloid were replotted as in Figure 5. From the slopes the U^* were obtained as a function of σ . As before this yields $U^* = -\gamma\sigma + U_0$. For Celluloid the results are $U^* = -5.9 \sigma + 62$ (kcal). Application of Equation [3a] using the α 's obtained from the original data give values of γ only some 20 to 40 percent of 5.9. Clearly Celluloid does not behave "normally" for the Zhurkov method where the γ 's from Equation [3a] or [3b] yield the same value.

A somewhat different analysis of the Celluloid data reveals thermodynamic functions not apparent in the preceding discussion. From Equation [1], for any fixed σ , the constant A may be obtained as a function of temperature. The results are presented in Figure 6 from which $A = 5.6 \times 10^{-34} \exp(63400/RT)$. The preexponential factor is 30 orders of magnitude from that obtained above (i.e., 5×10^{-4}). With Zhurkov materials, the preexponential factors do not differ for a similar analysis. The energy terms ($U_0 \approx 62 \approx 63.4$ kcal) are in good agreement considering the fact that data were extracted from the rather small figure of Reference 8.

Using the value $\tau_0 = 5 \times 10^{-4}$ and A's from Figure 6 and inserting these into Equation [3b], $A = \tau_0 \exp(U'_0/RT)$, where the prime is to distinguish from the above-determined U_0 . U'_0 may be obtained as a function of temperature shown in Figure 7, where $U'_0 = -130T + 62000$ cal. It appears then that $U'_0 = -130T + U_0$. It should be noted here that this is of the form $\Delta F = \Delta H - T\Delta S$.

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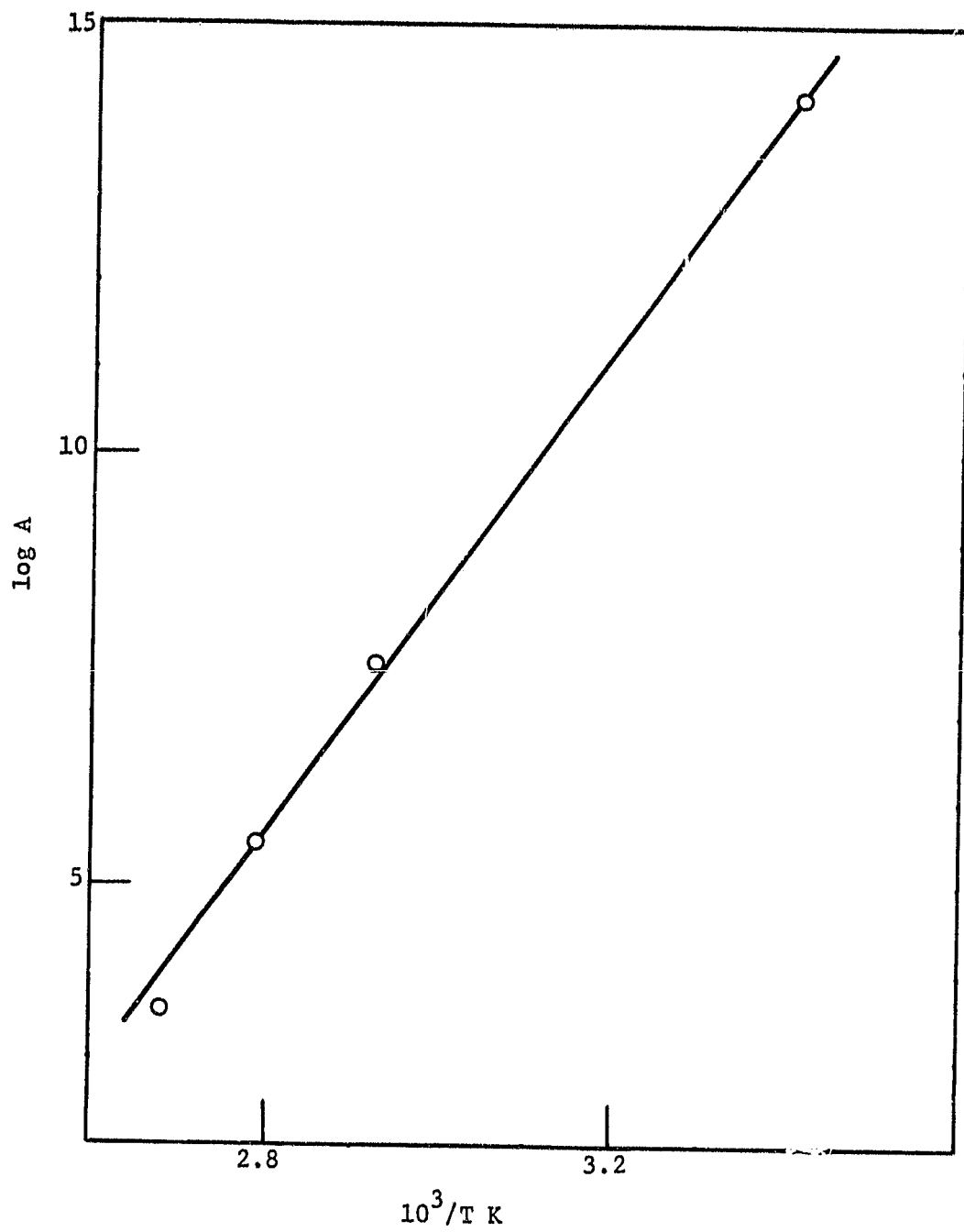


Figure V-6 The Constant A for Celluloid

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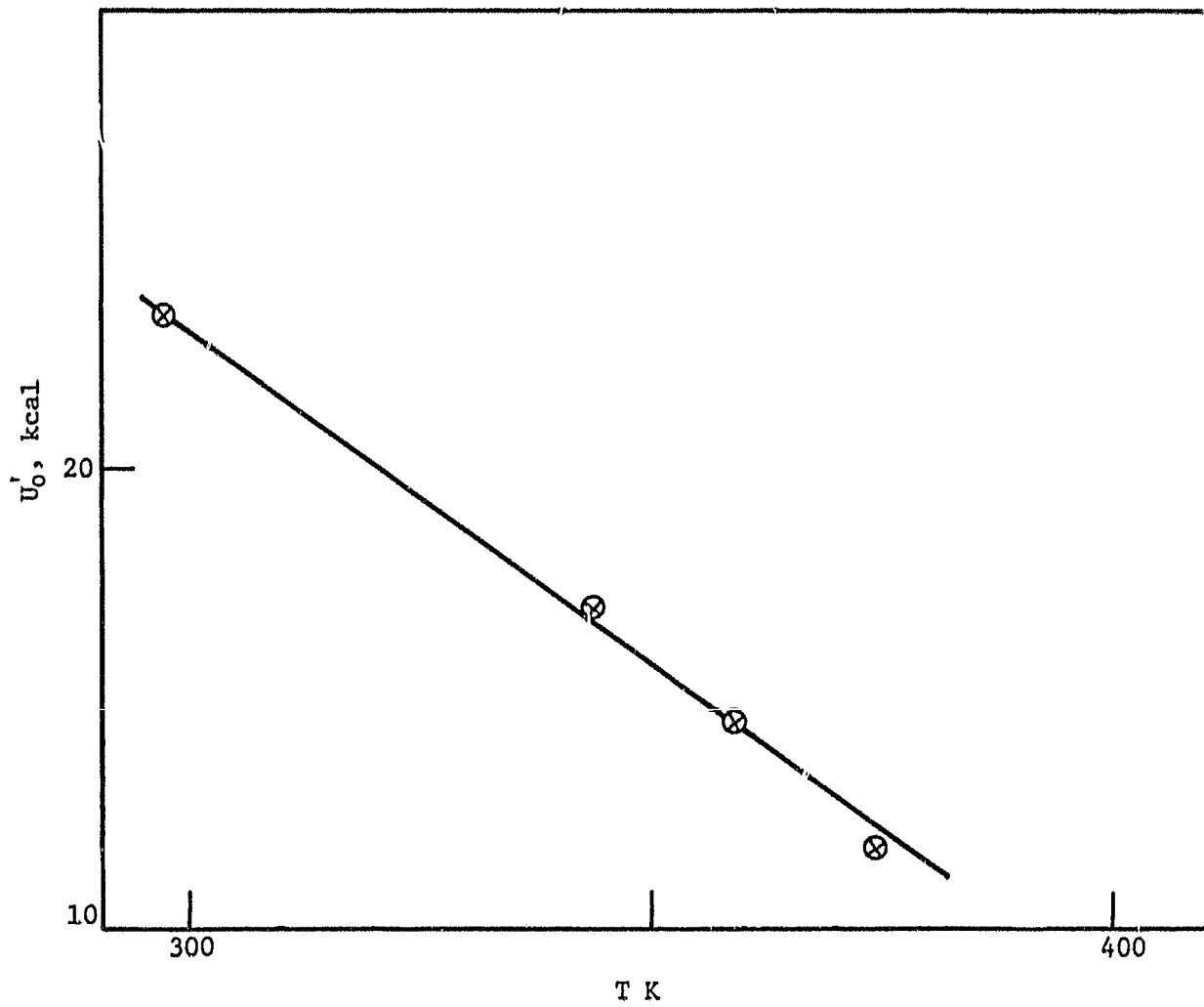


Figure V-7 Variation of the Energy Term in A

For these two different A's, i.e., $A = 5 \times 10^{-4} \exp (U_0/RT)$ and $A = 5.6 \times 10^{-34} \exp (U_0/RT)$, Zhurkov's Equation [1] yields two equations that must be resolved:

$$\tau = 5 \times 10^{-4} e^{U'_0/RT} e^{-\alpha\sigma}$$

and

$$\tau = 5.6 \times 10^{-34} e^{U_0/RT} e^{-\alpha\sigma}$$

Substituting for $U'_0 = -130T + U_0$

$$\ln \tau = -130/R + U_0/RT - \alpha\sigma + \ln \tau'_0$$

where τ'_0 should be the 5×10^{-4} value, and

$$\ln \tau = U_0/RT - \alpha\sigma + \ln(5.6 \times 10^{-34}).$$

Equating and solving for τ'_0

$$\tau'_0 = \tau_0 e^{130/R} = 5.6 \times 10^{-34} (3.27 \times 10^{28}) = 1.83 \times 10^{-5},$$

which is in reasonable agreement with 5×10^{-4} considering the available data.

It should be noted that the $\exp (130/R)$ is an entropy of activation(10). This also follows from the analogy between U_0 and ΔF mentioned above. Then U_0 is the enthalpy of activation ΔH and

$$\tau = 5 \times 10^{-4} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT} e^{-\alpha\sigma}$$

or

$$\tau = \tau_0 e^{\Delta F^\ddagger/RT} e^{-\alpha\sigma}$$

$$\tau = \tau_0 e^{(\Delta F^\ddagger - \gamma\sigma)/RT},$$

which is of course Zhurkov's Equation [2]. Thus for "normal" Zhurkov materials, where U_0 is obtained by extrapolation of $U(\sigma)$ to $\sigma = 0$, U_0 is to be identified with the free energy of a standard state.

In air, Lucite(11) and Delrin(12) behave in a manner similar to Celluloid, i.e., the pole depicted in Figure 4 is also some 9 to 10 orders of magnitude removed from Zhurkov-type materials ($\tau_0 \sim 10^{-13}$). They can be assessed in the same manner as above for Celluloid.

Accelerated tests for these kinds of materials can be carried out in the same manner as noted above for "normal" Zhurkov materials.

When Lucite and Delrin are tested under vacuum, the data for $\log \tau$ vs σ do not intersect at a common σ_0 as depicted in Figure 4. A series of parallel lines for the various temperature are observed. Similar results are observed for cellulose, acetate and polystyrene for both air and vacuum tests⁽¹¹⁾.

Figure 5 then is modified to Figure 8 when $\log \tau$ is considered as a function of temperature (Zhurkov's Equation [2]).

The existence of parallel slopes for $\log \tau$ vs σ may be understood by considering Figure 8:

$$\frac{d(\ln \tau)}{dT} = - \frac{U^*}{kT^2} = \text{constant}$$

$$\frac{\partial}{\partial \sigma} \left(\frac{d(\ln \tau)}{dT} \right) = \frac{\partial}{\partial \sigma} \left(- \frac{U_0 - \gamma \sigma}{kT^2} \right) = 0 ,$$

$$\frac{\partial}{\partial \sigma} U_0 = 0 \quad (\text{from definitions above}),$$

$$\frac{\partial}{\partial \sigma} \left(\frac{d(\ln \tau)}{dT} \right) = \frac{\partial}{\partial \sigma} \left(\frac{\gamma \sigma}{kT^2} \right) = 0 ,$$

$$\frac{\partial}{\partial \sigma} \left(\frac{\gamma \sigma}{kT^2} \right) = \frac{1}{kT^2} \left(\sigma \frac{\partial \gamma}{\partial \sigma} + \gamma \right) = 0 ,$$

$$\sigma \frac{\partial \gamma}{\partial \sigma} + \gamma = 0 ;$$

either $\gamma = 0$,

or $\gamma = f(\sigma)$.

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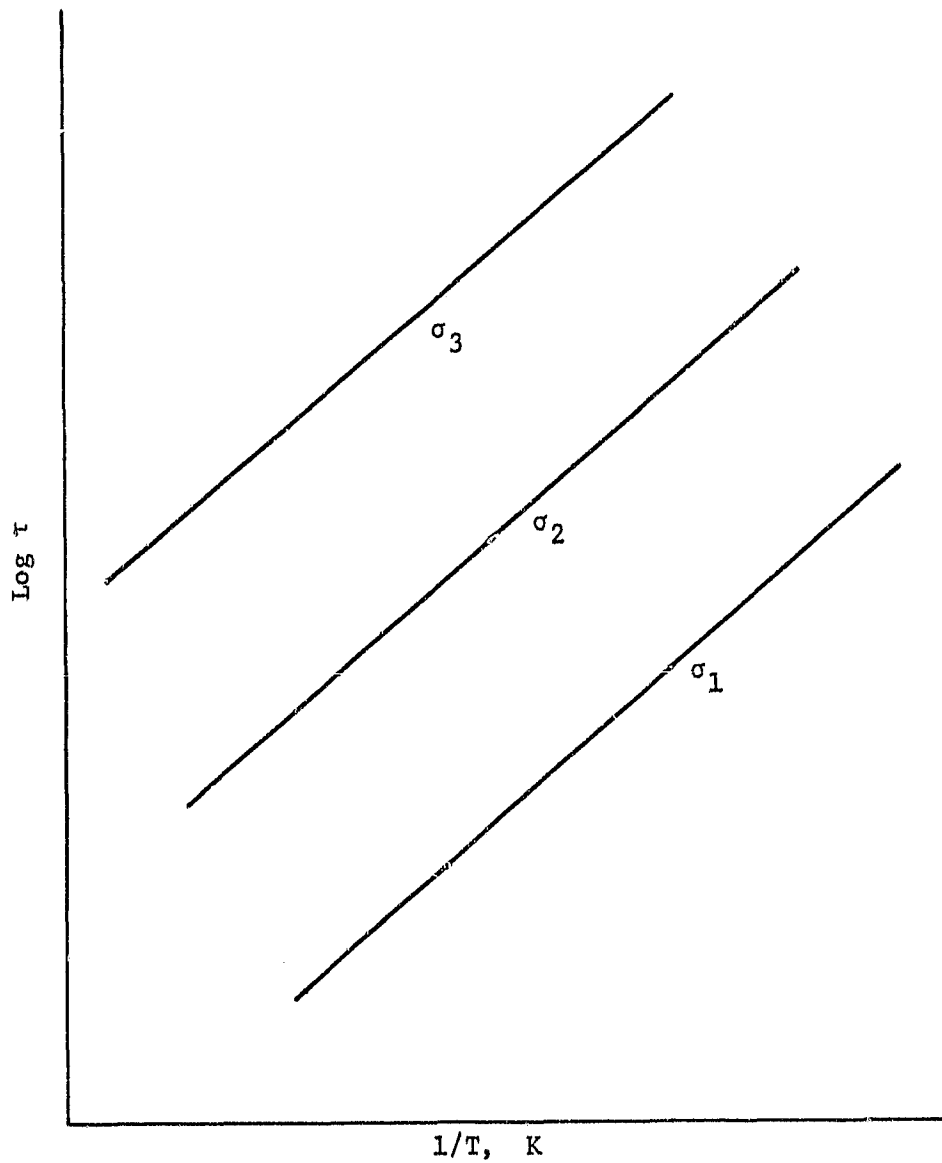


Figure V-8
Time to Rupture As a Function of Temperature for Materials Showing
Parallel Slopes for log τ vs σ

The following analysis shows that $\gamma = 0$. However, in filled polymers such as graphite/epoxy composites, it is shown in the next section shows that $\gamma = f(\sigma)$.

Because $\log \tau$ vs σ have parallel slopes, α is a constant, and for Lucite $\alpha = 3.36$ at any temperature. From results similar to those depicted in Figure 8, $U^* = 42.8$ kcals. An analysis similar to that depicted in Figure 5 yields

$$A = 8.2 \times 10^{-20} e^{U^*/RT}.$$

An entropy term on the order of $e^{13.8/R}$ will bring the preexponential factor in line with a Zhurkov τ_0 .

Analysis for τ_0 vs σ (shown in Fig. 9) yields

$$\tau_0 = 8.2 \times 10^{-20} e^{-3.36\sigma}.$$

Because $\alpha = 3.36$, then

$$\tau_0 = 8.2 \times 10^{-20} e^{-\alpha\sigma}.$$

Inserting A into Equation [1] and τ_0 into [2] and equating their logarithms shows $U^* = U_0 - \gamma\sigma$, and because U^* is constant (Fig. 8) it must be concluded that $\gamma = 0$ for materials showing parallel slopes for $\log \tau$ vs σ at various temperatures.

Finally, for results showing parallel slopes, Zhurkov's Equation [2] is simply

$$\tau = \tau_0 e^{U_0/RT}.$$

This conclusion was reached earlier⁽¹¹⁾ without detailed analysis. It has been shown⁽¹²⁾ that for such materials U_0 is essentially identical to the activation energies of thermal decomposition.

For these kinds of material behavior (i.e., parallel slopes), the accelerated tests are simpler to formulate because the temperature dependence can be obtained with fewer test points.

Zhurkov claimed that his equations were verified for both metals and nonmetals. For nonmetals, at least, their modifications must be considered when undertaking data analysis by his method. However, the approach can be used to devise quite simple and time-saving accelerated tests and warrants more attention than it has received.

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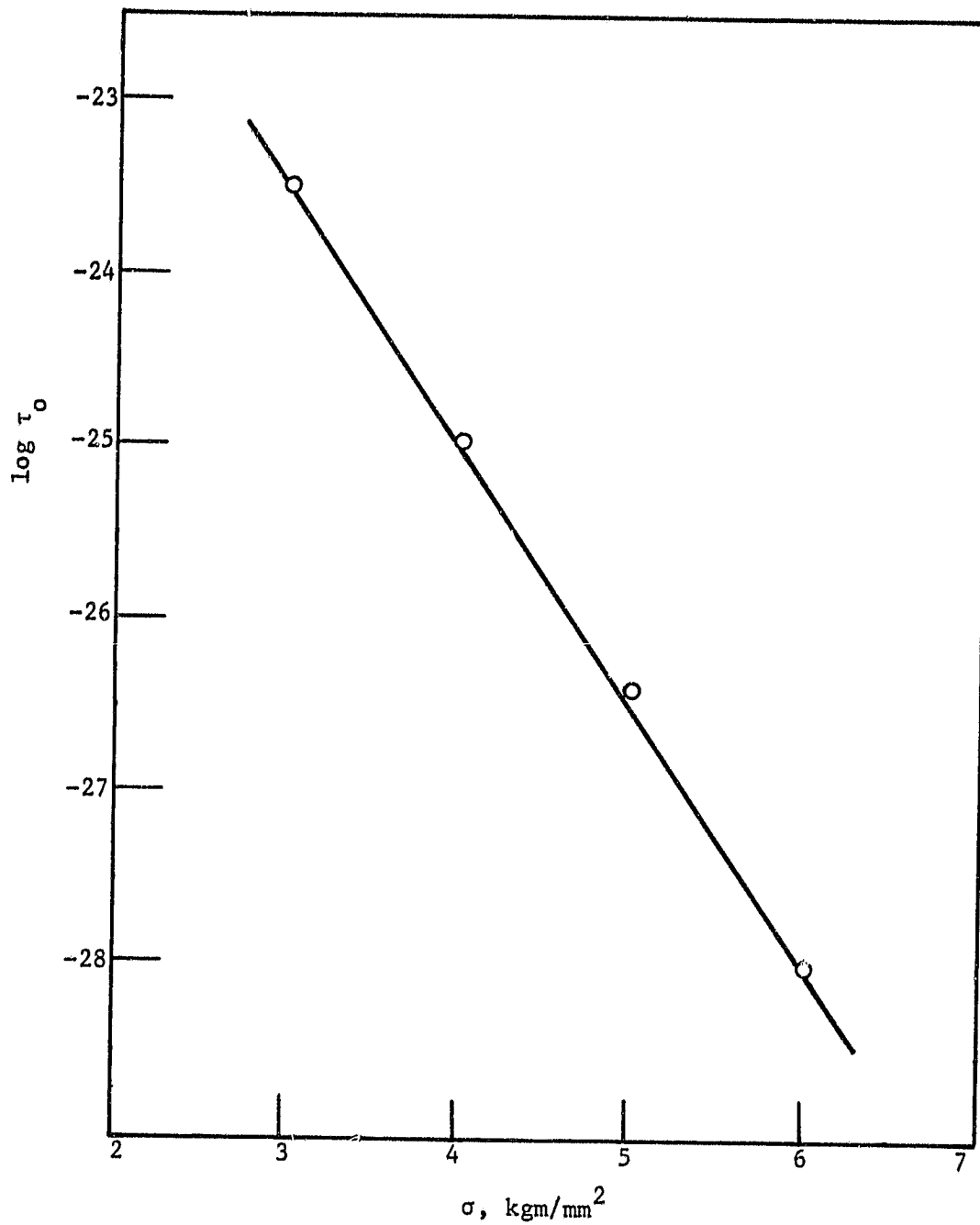


Figure V-9 τ_0 As a Function of σ for Lucite

The discussion most clearly indicates the kinetic rate theory basis of the approach. Zhurkov's energy term U_0 is to be associated with a standard state where this state is for $\sigma = 0$. This appears to be confirmed by the association of U_0 with the activation energy of thermal decompositions⁽¹¹⁾, where obviously $\sigma = 0$. (It would be instructive to study thermal decompositions of materials under load.) Since the Arrhenius rate constant is given by $k_T = Z \exp(-\Delta E/RT)$, the constant A in Zhurkov's Equation [1] appears to be $A = 1/k_T$ with $\tau_0 = 1/Z$. From absolute rate theory the rate constant is given by

$$k_T = (kT/h) e^{\Delta S^\ddagger / R} e^{-\Delta H^\ddagger / RT}$$

and therefore Z can be equated with $(kT/h) \exp(\Delta S^\ddagger / R)$. The $kT/h = \nu$ second⁻¹ is associated with vibrations in an "activated complex." Then $\tau_0 = 1/\nu$ (as defined by Zhurkov) ranges between $(1.6 - 1.2) \cdot 10^{-13}$. These considerations imply the absence of an entropy term in "normal" Zhurkov materials as the analysis has shown. For materials where $\tau_0 \neq 10^{-13}$, the entropy term appears to be contained within τ_0 .

Comparison of the behavior in air and in vacuum of Lucite⁽¹¹⁾ and Delrin⁽¹²⁾ shows that for some polymers γ should be associated with surface phenomena as suggested in the next section for the graphite/epoxy interface. If this conjecture is viable, then from studies of such materials it may be possible to determine the activation thermodynamics of crack growth. However the true role of γ must await further work.

C. ACCELERATED TESTING OF COMPOSITES

Modern technology is making extensive use of composites, especially in aircraft and space structures. For long-duration performance, the designer needs to know how long a composite under load can be expected to last in a given situation. Real-time tests are clearly impractical in both time and money. The obvious solution to this problem is to use accelerated test methods to predict the lifetime of the composite. A review of the literature shows a paucity of work on accelerated testing in general, and particularly for composites. Brinson and his coworkers⁽¹³⁾ have tried the time-temperature superposition method and Chiao⁽¹⁴⁾ has used the creep rupture method of Zhurkov.⁽⁷⁾ Both methods were developed before the advent of composite materials and have shown only modest success when applied to composites. The Zhurkov method's success had been modest because of a lack of understanding of its limitations and modifications.

It is the purpose of this section to show that the Zhurkov method can also be applied to dynamic tension and to cyclic loading and provides a viable approach to accelerated testing of composites.

The following data (obtained from the literature) will show a straightforward application of Zhurkov's Equation [1] for dynamic tension of glass fiber and cyclic loading for glass/polymer, metal matrix and graphite/epoxy composites. Temperature data were available for only the latter.

Zhurkov developed his creep rupture method by successfully applying his relationships to over 50 different metals and polymers. The Russian literature indicates that his method is unquestioned there. Outside Russia the method has received little attention and, as developed in the following sections, we will show how unfortunate this oversight has been.

The relationships of Zhurkov are as before

$$\tau = Ae^{-\alpha\sigma} \text{ (at constant temperature)}$$

$$\tau = \tau_0 e^{U^*/kT} \text{ (at fixed } \sigma \text{)}.$$

According to Zhurkov when a material behaves according to Equations [1] and [2], τ_0 is considered to be the period of natural oscillation in the solid ($\sim 10^{-12}$ seconds) and γ is a constant that depends on the structure of the material. Then Equations [1] and [2] are related through $A = \tau_0 \exp(U_0/kT)$ and $\alpha = \gamma/kT$.

For an accelerated test at some temperature of interest, a few data points at relatively high loads (i.e., short failure times) will permit evaluation of the constants in Equation [1]. Then Equation [1] can be used to predict failure times at low loads where the failure times are long. With high load tests at two, or at the most three, temperatures, the constants of Equation [2] can be evaluated. Failure times can then be predicted at any temperature and load. The results below show the efficacy of Equation [1] to a variety of composites. Temperature data were found only for the graphite/epoxy composites.

1. Dynamic Tension

Figure 10 shows results for Suprasil-2 glass fibers under static and dynamic tension. Zhurkov's Equation [1] may be applied to both conditions. Taking a few data points at relatively high loads (short rupture times) will permit prediction of lifetime at low loads where the rupture times would be very much longer.

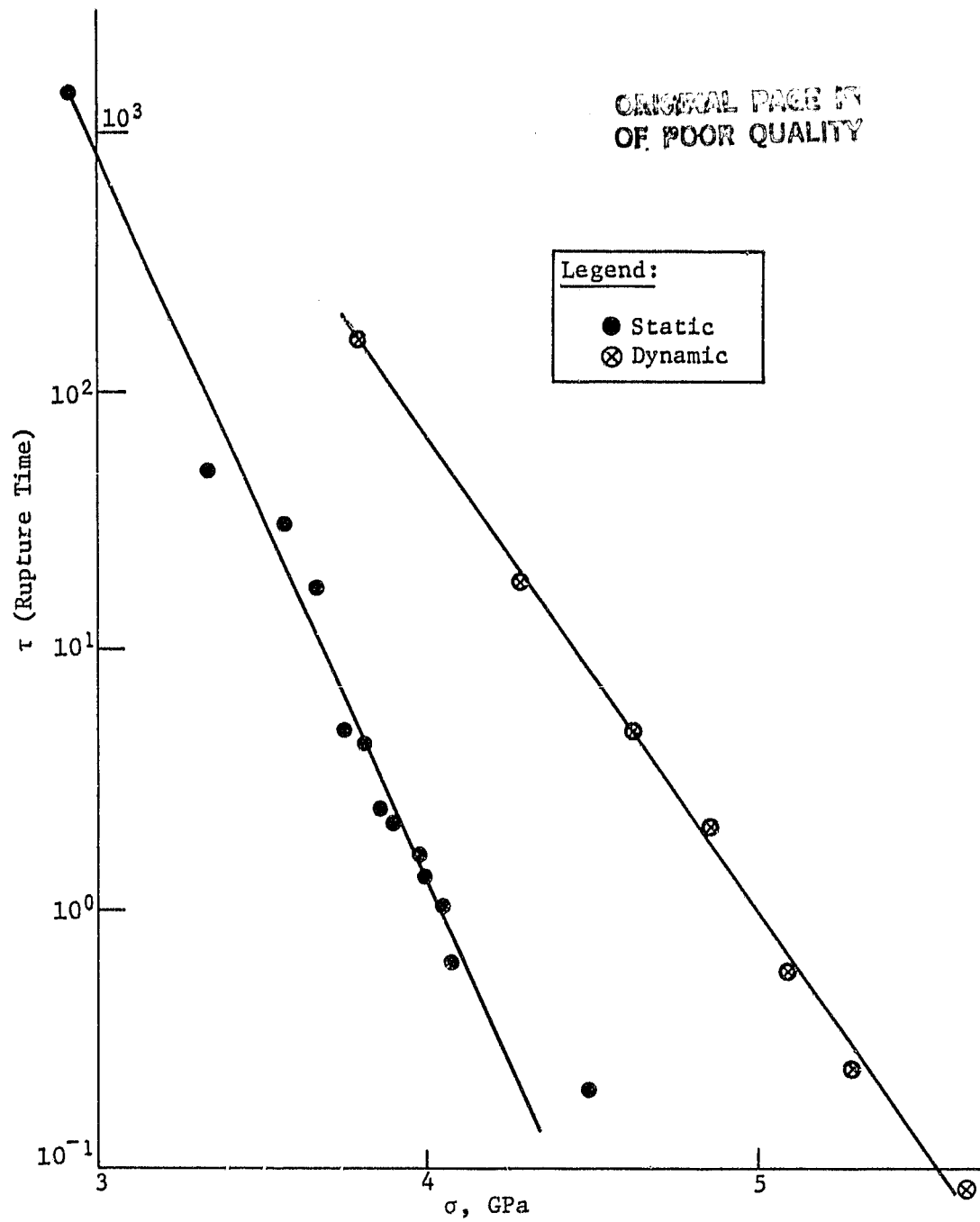


Figure V-10 Static and Dynamic Rupture of Suprasil-2 Glass Fibers

2. Cyclic Loading

Figure 11 shows some results for glass/polymer composites under cyclic loading. The cycles to failure have been labeled as τ to simplify comparison with Equations [1] and [2]. Because temperature data were not available, only Zhurkov's Equation [1] can be considered. The applicability of the equation is clearly demonstrated.

Figure 12 shows cyclic loading data for metal matrix composites. Again the applicability of Zhurkov's Equation [1] is apparent.

In Reference 19 considerable data were taken for unidirectional and angle ply graphite/epoxy composites under cyclic loading. Figure 13 compares the results for 30-degree unidirectional and ± 30 -degree angle plies. Similar results were obtained for the other plies of Reference 19. The existence of parallel slopes for $\log \tau$ vs σ has been discussed in the detailed development of the Zhurkov method and its modifications given in the next section.

Figures 14 and 15 show the results for σ and α as a function of ply angle for unidirectional and angle plies, respectively. Simple algebraic manipulation shows the Zhurkov's $\gamma = f(\sigma)$, whereas for unfilled polymers with parallel slopes this coefficient is zero. Here then, γ must be associated with the fiber and/or fiber matrix interface.

Again the utility of Zhurkov's Equation [1] is apparent. The use of Equation [2] is enhanced because data at only one other temperature are required for predictions at any other desired temperature.

These results show that Zhurkov's approach can be used to devise accelerated tests of composites with a minimum of test data for such parameters as static and dynamic tension and cyclic loading. Zhurkov's Equation [1] can be used at relatively high loads (short failure times) to obtain failure times at loads at any temperature of interest. By taking a few data points at one or two other temperatures, the spectrum of failure times can be expanded to temperatures not easily accessible.

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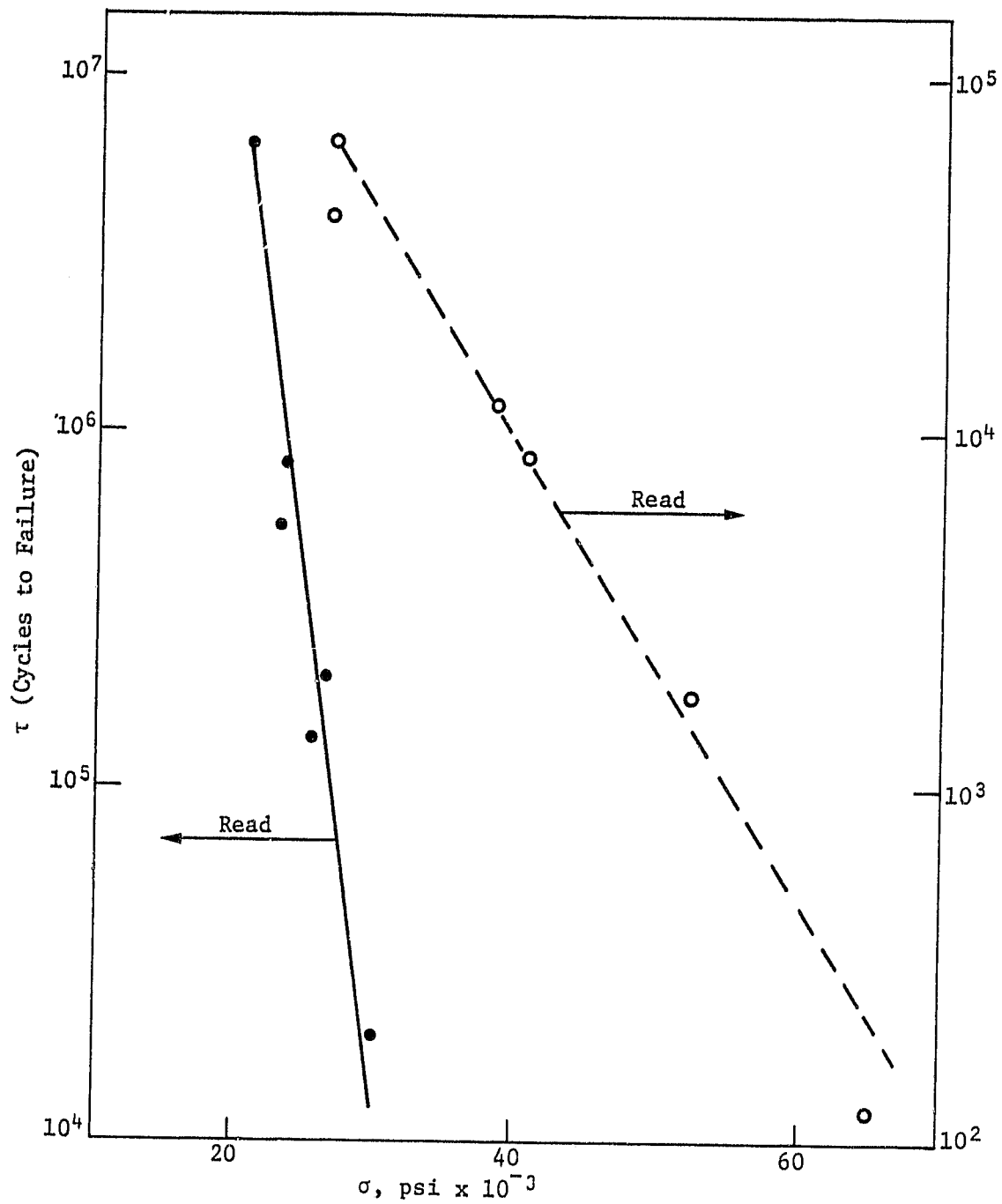


Figure V-11 Glass Composites

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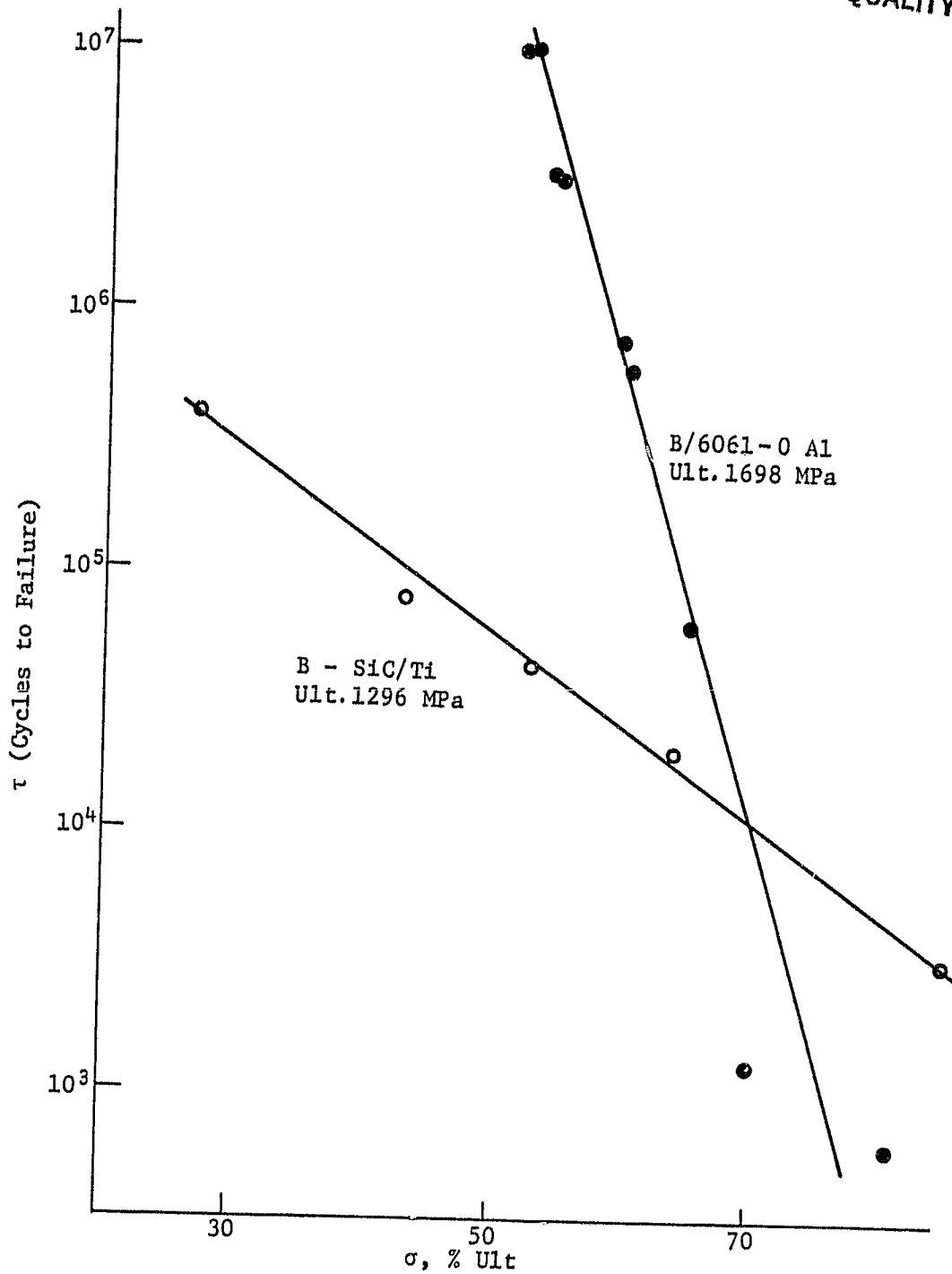


Figure V-12 Metal Matrix Composites

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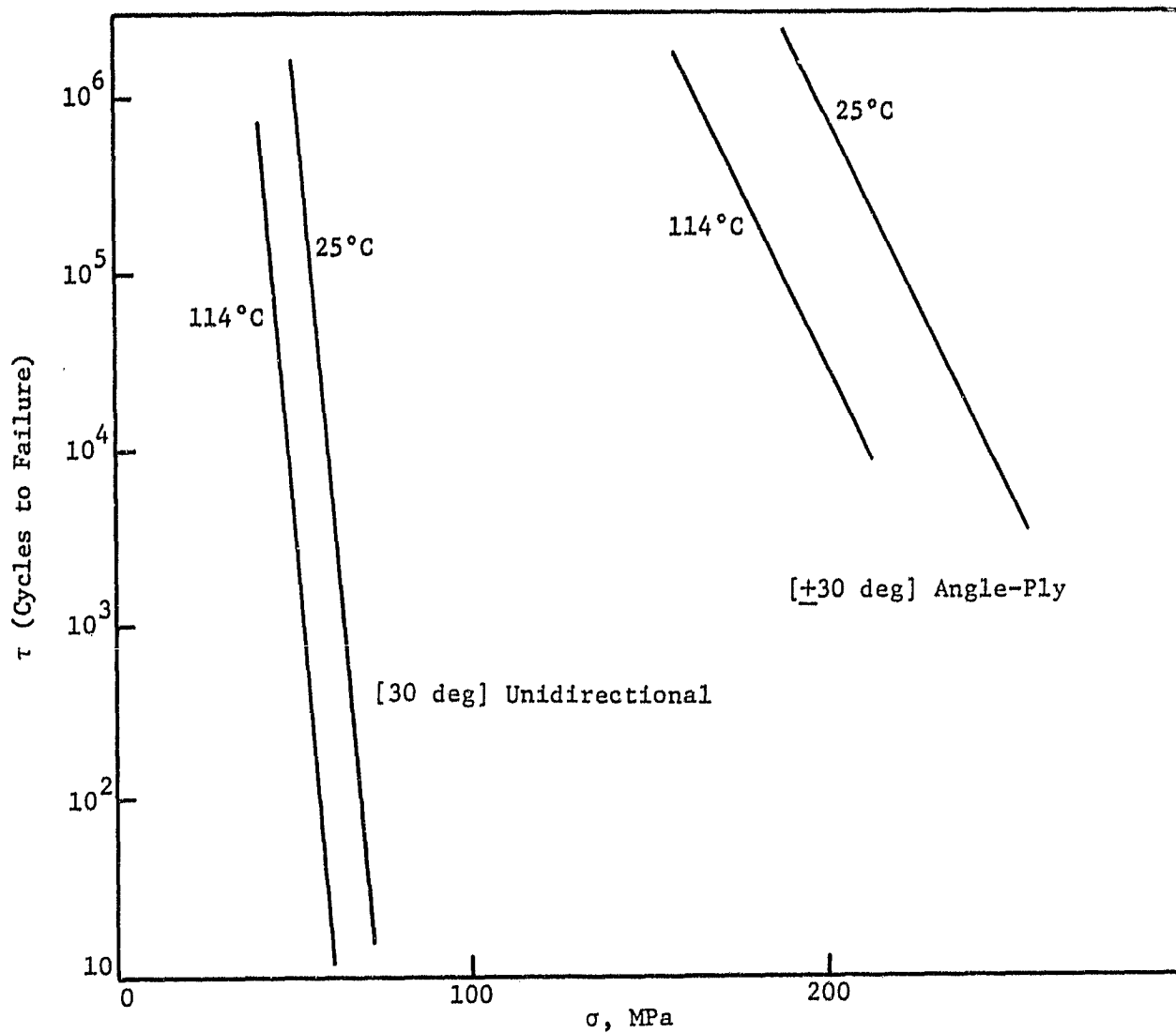


Figure V-13 Graphite/Epoxy Composite

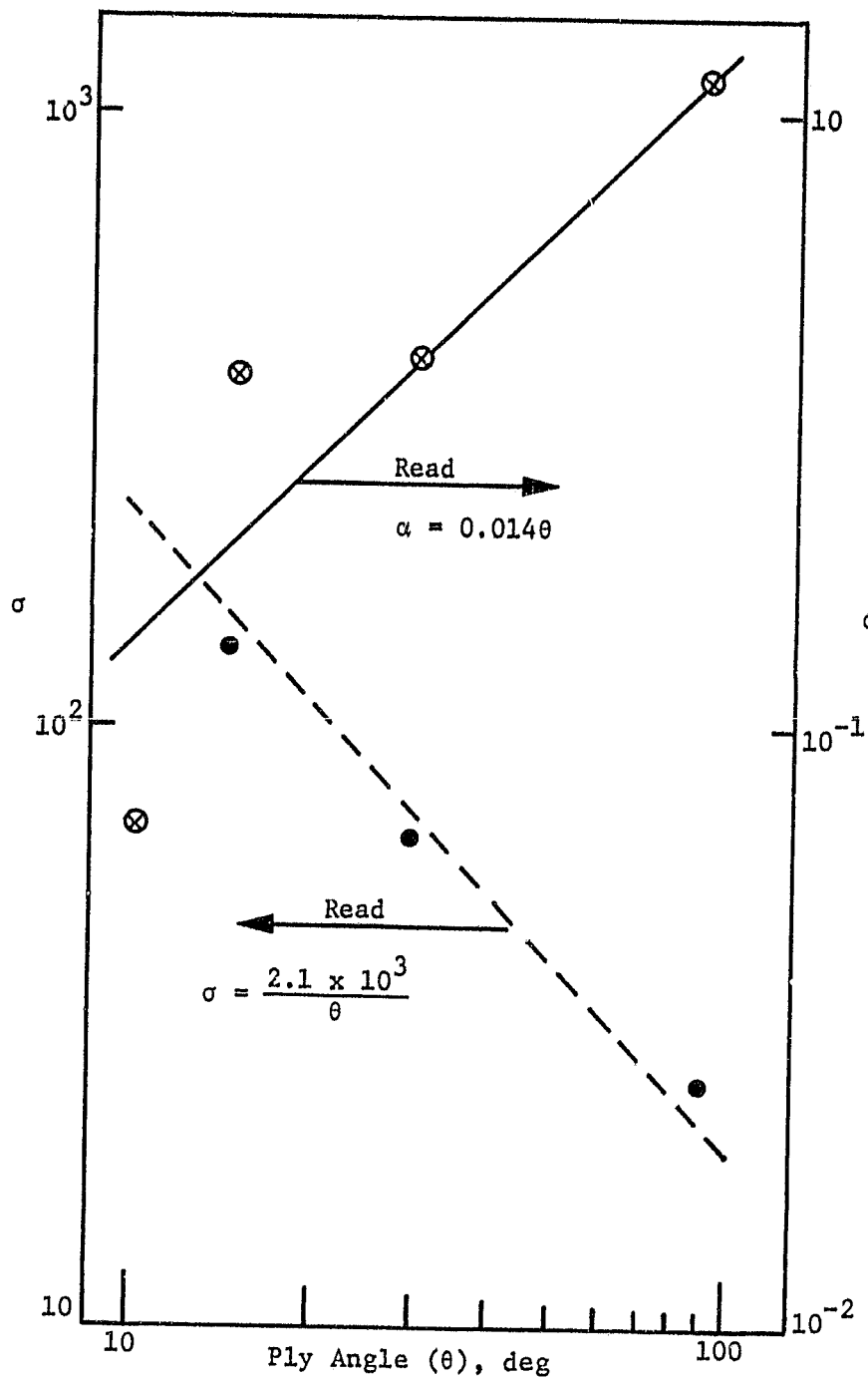


Figure V-14
Unidirectional Off-Axis Laminate (Developed from Ref 19 Data)

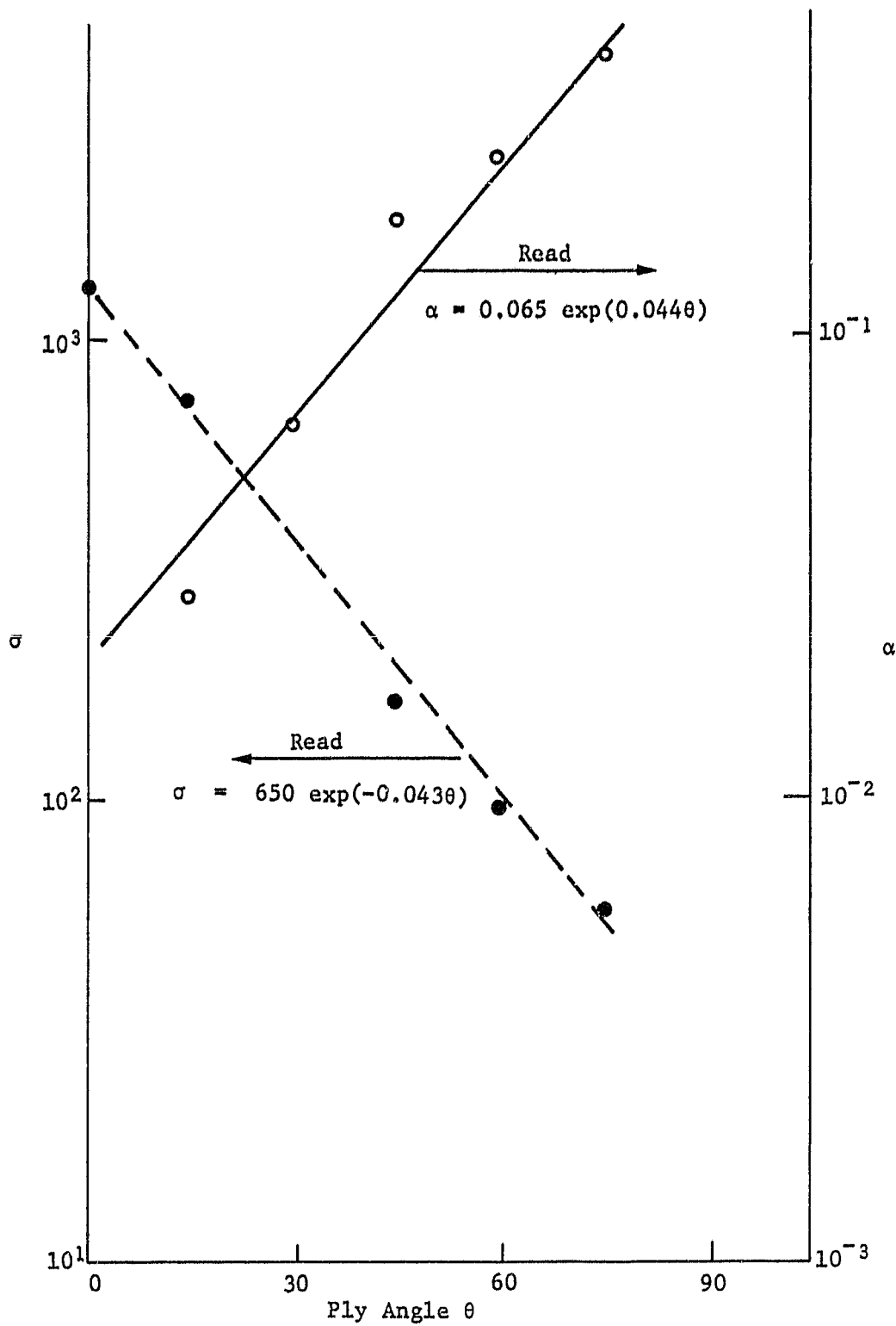


Figure V-15 Angle Ply Laminates

D. THERMODYNAMICS OF CREEP RUPTURE

The discussion in Section V.B presented the well-known Zhurkov relationship for creep rupture. When experimental results of $\log \tau$ (time to rupture) vs stress σ at several temperatures are extrapolated to large stress, they intersect at a common pole τ_0 at a critical stress σ_k . Well-behaved Zhurkov materials have poles near 10^{-13} seconds. Other materials show poles with $\tau_0 \gg 10^{-13}$ seconds. When these materials are studied in vacuum, a different behavior is observed. The earlier discussion showed that an entropy term, not present in well-behaved materials, could be justified by manipulation of the results obtained in air. The present discussion is a more rigorous development of these results and shows that a premature (and probably erroneous) conclusion was drawn in the earlier discussion for results in vacuum.

The following abbreviated development is after Reif.(20) For a macroscopic system characterized by one or more external parameters, the number of quantum states in the energy interval between E and $E + \delta E$ depends not only on the energy but also on the particular values of the external parameters. For simplicity, for one external parameter $\Omega = \Omega(E, x)$. The energy of each state E_n depends on the value assumed by the external parameter; therefore

$$dE_n = \frac{\partial E_n}{\partial x} dx = X_n dx.$$

For the mean value of X

$$[4] \quad \bar{X} dx = \frac{\partial E_n}{\partial x} dx = dW,$$

or the macroscopic work done on the system when the external parameter is changed quasi-statically (e.g., thermodynamically reversible), is equal to the mean increase in the energy of the system. It can be seen that \bar{X} is a generalized force, conjugate to the external parameter and, in general, may have any dimension (i.e., units).

The change in the number of states Ω as a function of the work done on the system is given by

$$\left(\frac{\partial \ln \Omega}{\partial x} \right)_E = - \frac{\bar{X}}{kT}.$$

With the Boltzmann-defined entropy, $S = k \ln \Omega$, this becomes

$$[5] \quad \left(\frac{\partial S}{\partial X} \right) = - \frac{X}{T},$$

which is the desired development for the present discussion.

Zhurkov developed his well-known creep rupture relationship from the time dependence of strength under unidirectional tension. He successfully applied it to a variety of metals and nonmetals. The relationship is defined by

$$[6] \quad \tau = \tau_0 e^{(U_0 - \gamma \sigma) / kT}$$

where the time to rupture τ is a function of the activation energy for the process U_0 less the work done $\gamma \sigma$ on the system. The constant γ depends on the nature of the structure of the material. When experimental results of $\log \tau$ vs stress σ at several temperatures are extrapolated to large σ , they intersect at a common point, the pole τ_0 and the critical stress σ_k . A simple manipulation of Equation [6] shows $U_0 = \gamma \sigma_k$. The τ_0 is considered to be $1/\nu$ where ν is a vibrational frequency of bonded atoms in the solid.

Work done at constant volume becomes a definite thermodynamic property of the system (i.e., a definite integral) so the work dW (Equation [4]) becomes

$$dW = \gamma d\sigma + \sigma d\gamma = X dx.$$

With γ being constant, Equation [5] can be written as

$$[7] \quad T \Delta S = \gamma (\sigma_k - \sigma).$$

From energy conservation, the heat absorbed dQ by a system can be used to increase energy ΔE and do work. Therefore

$$T \Delta S = dQ = \Delta E + \text{work}.$$

In this quasi-static development, the work may be taken as the negative of the work being done on the system and, from Equation [7]

$$[8] \quad T \Delta S = \gamma (\sigma_k - \sigma) = dQ = \Delta E - \gamma \sigma.$$

This is just the Helmholtz "work function" relationship $\Delta A = \Delta E - T \Delta S$ when ΔA is taken as $\gamma \sigma$. With the Zhurkov-defined $U_0 = \gamma \sigma_k$, substitution of $\sigma = 0$ or $\sigma = \sigma_k$ shows $U_0 = \Delta E$. In a given isothermal process, ΔA is the maximum (reversible) work available. From Equation [7], when $\sigma = \sigma_k$ the process is adiabatic or the rupture of the specimen takes place before any absorption of heat from the reservoir. When there is no significant $P \Delta V$ work, such as with solids, the Gibbs "free energy" $\Delta F = \Delta H - T \Delta S$ may be used for the Helmholtz relationship without loss of rigor. The association of U_0 with ΔH was shown earlier by a less rigorous development.

Thermodynamically Zhurkov's relationship can be written

$$\tau = \tau_0 e^{(U_0 - \gamma \sigma)/kT} = \tau_0 e^{\gamma(\sigma_k - \sigma)/kT} = \tau_0 e^{(\Delta H - \Delta F)/kT} = \tau_0 e^{\Delta S/k}.$$

Thus at any stress level less than σ_k , the time to rupture is determined by the entropy change in the solid.

For some materials the pole τ_0 is many orders of magnitude removed from $\tau_0 \sim 10^{-13}$ seconds as found for well-behaved Zhurkov materials. Celluloid has a $\tau_0 \sim 10^{-4}$ and Lucite and Delrin have τ_0 of 5×10^{-3} and 2.5×10^{-3} seconds, respectively. (11,12)

When the usual Zhurkov determination for γ is carried out, γ is not independent of temperature but rather is found to be $\gamma = -\frac{a}{T} + \frac{b}{T}$ where $\frac{a}{T}$ and $\frac{b}{T}$ are constants. For Lucite and Delrin, γ becomes a zero at 350 and 380K, not unreasonable values for their glass temperatures (no information was found for T_g of Celluloid).

For these kinds of materials, the entropy becomes

$$[9] \quad \Delta S = -a(\sigma_k - \sigma) + \frac{b(\sigma_k - \sigma)}{T}.$$

Because the second term on the RHS has already been defined as for the quasi-static process, the ΔS of Equation [9] is the entropy change for a nonquasi-static process. For a quasi-static process, the entropy is given by

$$\Delta S = S_f - S_0 = \int_{qs}^f \frac{dQ}{T},$$

and for a nonquasi-static (thermodynamically irreversible) process

$$\Delta S = S_f - S_0 > \int_{nqs}^f \frac{dQ}{T}$$

where T now refers to the temperature of the reservoir. If a quasi-static path is constructed for the nonquasi-static process, the entropy change can be determined as

$$\Delta S = \int_{qs} \frac{dQ}{T} = \int_{nqs} \frac{dQ}{T} + \Delta S_i$$

Then Equation [9] is

$$\int_{nqs} \frac{dQ}{T} = -\Delta S_i + \int_{qs} \frac{dQ}{T}$$

and the extra term in Equation [9] is the discrepancy between the quasi-static and nonquasi-static processes. Clearly for these kinds of materials, the rupture process is fundamentally different from well-behaved Zhurkov materials, with the rupture process being inherently nonquasi-static.

For these materials the Zhurkov relationship can be written as

$$\tau = \tau_0 e^{-\Delta S_i / k} e^{\Delta S / k} = \tau'_0 e^{\Delta S / k} = \tau'_0 e^{(\Delta H - \Delta F) / kT} = \tau'_0 e^{(U_0 - \gamma \sigma) / kT}.$$

A similar result was found in a previous section. There it was stated that the experimentally determined $\tau_0 \gg 10^{-13}$ seconds could be corrected by a fixed entropy term. That this cannot be strictly true is shown in the present development where it is found that the correction term ΔS_i is a function of σ . However the a of the correction term is quite small (0.0134 for Celluloid, 0.074 for Lucite and 0.037 for Delrin) so the earlier contention of a fixed term is not entirely incorrect.

When Lucite and Delrin are studied under vacuum (11,12) the slopes of $\log \tau$ vs σ differ considerably from those obtained in air. It was argued that in vacuum the slopes at various temperature became parallel, i.e., no common σ_0 and σ_k . The development here shows that this is probably not true, and that the premature conclusion was based on a too narrow range of temperature used in the vacuum studies. From the development here it must be concluded that these materials revert to well-behaved Zhurkov-type materials, i.e., the finite ΔS_i found in air becomes zero in vacuum. An obvious consideration is that this is a surface phenomenon associated with a difference in crack behavior in the presence of air.

VI. CONCLUSIONS AND RECOMMENDATIONS

The Hercules graphite/epoxy specimens under in-plane shear showed an increase in modulus after a year under thermal-vacuum exposure. Although the changes in ultimate strength for the AS4/3501-6 specimens are not considered as significant, the changes for HMS/3501-6 were large enough to be considered significant. When the resin content of both types of material is considered, the decrease in ultimate strength may be associated with the smaller amount of resin. We recommend that this suggestion be validated by more testing with in-plane shear studies.

In all testing of composites, a much larger number of specimens must be tested than has been possible to date.

The discussion on the effects of irradiation in Section V.A shows the importance of the MSFC/Martin Marietta approach to such studies; namely, specimens must not be exposed to air after irradiation until testing is complete. With the paucity of literature data,⁽¹⁾ it is of prime importance that charged particle irradiation be subjected to all candidate materials for space applications.

Zhurkov's approach to the strength of solids can be used for predictive modeling or accelerated testing.^(8,11,12) The fundamentals of the method (not previously discussed in the literature) are discussed in Sections V.B and V.D. Section V.C demonstrate the application to composite materials. It would be of considerable value to study the surface effects noted between ambient and vacuum tests as discussed in V.B and V.D. Such testing would clarify the apparent discrepancy of results obtained under these two conditions. This would also contribute to the understanding of possible surface or interface effects in composites as discussed in Section V.C. Because the Zhurkov method is the simplest approach to prediction, the information developed would lead to a very high degree of confidence in the method. We recommend that such studies be considered.

The results in Section V.C are primarily of cyclic testing analyzed by the Zhurkov approach. This analysis has not been previously shown. Cyclic tests at several temperatures would be of great importance to establish the validity of the Zhurkov method for cyclic testing.

For consideration at a later date it would be of value to study the effects of irradiation on specimens while under load as discussed in Section V.A.

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